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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

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TRANSMITTAL LETTER TO THE UNITED STATES

DESIGNATED/ELECTED OFFICE (DO/EO/US)

CONCERNING A FILING UNDER 35 U.S.C. 371

Mueller-41

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

10/019795

INTERNATIONAL APPLICATION NO.

PCT/DE00/02138

INTERNATIONAL FILING DATE

5 July 2000

PRIORITY DATE CLAIMED

6 July 1999

TITLE OF INVENTION

Method of Producing Aluminum Hydroxides by Precipitating Aluminum Salts in the Presence of Seed Crystals
[as amended]

APPLICANT(S) FOR DO/EO/US

Rainer Gloeckler and Arnold Meyer

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

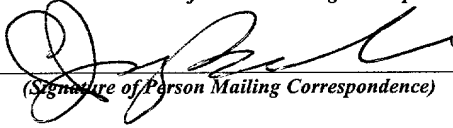
1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☒ Certificate of Mailing by Express Mail
23. ☐ Other items or information:

10/019795

1013 331107710 04 JAN 2002

CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)			Docket No.
Applicant(s): Rainer Gloeckler and Arnold Meyer			Muller-41
Serial No. To Be Assigned	Filing Date Herewith	Examiner To Be Assigned	Group Art Unit To Be Assigned
Invention: Method of Producing Aluminum Hydroxides by Precipitating Aluminum Salts in the Presence of Seed Crystals [as amended]			
I hereby certify that the following correspondence:			
Transmittal Letter to the DO/EO/US Concerning a Filing Under 35 USC 371 and all references enclosures			
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is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under			
37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231 on			
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
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In re Application of:	§	Attorney Docket No.: Muller-41
	§	
Rainer Glockler and Arnold Meyer	§	
	§	
Int'l. Appln. No.: PCT/DE00/02138	§	
	§	
Int'l. Filing Date: 5 July 2000	§	
	§	
Priority Date: 6 July 1999	§	
	§	
U.S. Serial No.: To Be Assigned	§	
	§	
U.S. Filing Date: Herewith	§	
	§	
For: <i>Method of Producing Aluminum</i>	§	
<i>Hydroxides by Precipitating</i>	§	
<i>Aluminum Salts in the Presence</i>	§	
<i>of Seed Crystals</i>	§	
[as amended]	§	

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Kindly amend the above-identified application as follows:

In the Specification

On page 1, in lines 1-2, kindly delete the title and insert therefor the following new title:

METHOD OF PRODUCING ALUMINUM HYDROXIDES BY PRECIPITATING
ALUMINUM SALTS IN THE PRESENCE OF SEED CRYSTALS

20040104 0400

On page 1, after the title and before line 4, please insert the following new heading and subheading:

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

On page 1, at line 6, please insert the following new subheading:

DESCRIPTION OF THE PRIOR ART

On page 2, at line 16, please insert the following new heading:

SUMMARY OF THE INVENTION

On page 2, at line 25, please insert the following new heading:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the Claims

Please cancel Claims 1-8.

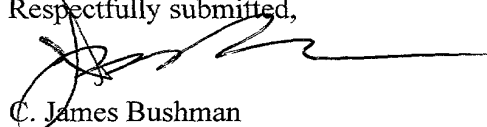
Please add the following new claims, 9-20:

9. A procedure for manufacturing boehmitic and/or pseudo-boehmitic alumina by precipitating basic and/or acidic aluminum salts, comprising precipitating said salts from an aqueous medium containing the following as the crystal nuclei:
 - (a) 0.1 to 5 % w/w of alumina hydrates and/or aluminas relative to the precipitated alumina hydrates and computed as Al_2O_3 , wherein the crystal nuclei (a) in the medium have an average diameter of 20 to 150 nm.

10. A procedure for manufacturing alumina hydrates by precipitating basic and/or acidic aluminum salts, comprising precipitating said salts from an aqueous medium containing the following as the crystal nuclei:
 - (b) 0.1 to 5% w/w of organic polymers/oligomers relative to the precipitated alumina hydrates and computed as Al_2O_3 , which form latices in the medium, wherein the crystal nuclei (b) in the medium have an average diameter of 12 to 250 nm.
11. A procedure according to any one of claims 9 or 10 wherein the average diameter is from 50 to 100 nm.
12. A procedure according to any one of claims 9 or 10, wherein crystal nuclei in an amount of 0.5 to 2 % w/w relative to the precipitated alumina hydrates and computed as Al_2O_3 are used for precipitation.
13. A procedure according to any one of claims 9 or 10, wherein the crystal nuclei are prepared in an aqueous, acidic solution and one or more basic aluminum salts and one or more acidic aluminum salts are jointly added.
14. A procedure according to claim 10, characterized in that polyacrylic acids, polymethacrylic acid, polyacrylates, polystyrenes, polyvinyl acetates, polyvinyl versalates and their mixtures or copolymers are used as organic polymers.
15. A procedure according to any one of claims 9 or 10, characterized in that alkali aluminates, earth alkali aluminates or aluminum hydroxy salts are used as the basic aluminum salts.
16. A procedure according to any one of claims 9 or 10, characterized in that aluminum sulfate, aluminum nitrate, aluminum chloride or aluminum formiate are used as the acidic aluminum salts.
17. A procedure according to any one of the claims 9 or 10, characterized in that the bulk of the alumina hydrate is precipitated at a pH value of 5 to 9.

18. A procedure according to claim 17 wherein the pH value is from 6 to 8.
19. A boehmitic alumina and/or pseudo-boehmitic alumina with a pore volume of 1.25 to 1.6 ml/g and an average pore radius of 6 to 12 nm, each relative to a determination based on pore radii of 0 to 100 nm, at a crystallite size, determined on the 120 reflex, of 3 to 5 nm, manufactured according to a procedure of any one of claims 9 or 10.
20. A procedure for manufacturing boehmitic and/or pseudo-boehmitic alumina by precipitating basic and/or acidic aluminum salts comprising precipitating said salts from an aqueous medium containing the following crystal nuclei:
 - (a) 0.1 to 5 w/w of alumina hydrates and/or aluminas relative to the precipitating alumina hydrates and computed as Al_2O_3 wherein the crystal nuclei (a) in the medium have an average diameter of 20 to 150 nm and,
 - (b) 0.1 to 5% w/w of organic polymers/oligomers relative to the precipitated alumina hydrates and computed as Al_2O_3 , which form lattices in the medium, wherein the crystal nuclei (b) in the medium have an average diameter of 12 to 250 nm.

Respectfully submitted,


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CERTIFICATE OF EXPRESS MAILING

I, C. James Bushman, hereby certify that this correspondence and all referenced enclosures are being deposited by me with the United States Postal Service as Express Mail with Receipt No. EL715550167US in an envelope addressed to: Box PCT, Assistant Commissioner for Patents, Washington, DC 20231, on January 4, 2002.

By: 

D-99 004 PCT

Application as originally filed

Method for Producing Alumina Hydrates by Precipitating Aluminum Salts in the Presence of Crystal Nuclei

5 The invention relates to a method for producing alumina hydrates by precipitating aluminum salts in the presence of crystal nuclei of a specific size.

10 Known in the art are procedures for manufacturing boehmitic alumina or alpha-aluminum oxide monohydrates by neutralizing basic aluminate solutions, e.g., with sulfuric acid or acidic aluminum salt solutions. In this case, the alumina hydrates are generally precipitated at a pH value of between 4.5 and 7. However, the literature also describes procedures in which the alumina hydrates are precipitated at a pH of 7 to 10.

15 The use of crystal nuclei during the precipitation of alumina is also known. In the procedure described in DE 21 25 625-C2, a sodium aluminate solution is reacted with nitric acid in a first boiler, precipitated in a second boiler, wherein a partial flow is removed from the latter and routed to the first boiler. According to the procedure described in DE 21 25 625-C2, pore volumes of up to 0.33 cm³/g are obtainable.

20 US 4,154,812 describes a procedure for the manufacture of alumina hydrates that involves 5 phases:

- 25 1. Formation of crystal nuclei from an aqueous aluminum salt solution by adding aluminum sulfate in water and setting a pH of 2 to 5.
2. Precipitation of the boehmitic alumina by setting a pH value of between 7 and 8 via the simultaneous addition of basic aluminate and acidic aluminum salt solutions.
- 30 3. Setting of a pH value of between 9.5 and 10.5 by adding a corresponding quantity of aluminate solution.
4. Repeated stirring of the alumina suspension.
5. Filtration of the suspension and washing of the filter cake.

35 The procedure according to US 4,154,812 is characterized by the observance of defined pH values and temperatures (54 to 82 °C) during specific phases of the reaction.

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The boehmitic alumina obtainable according to this procedure exhibit a pore volume (0-60 nm) of less than or equal to 0.82 ml/g after an activation (400 °C for 30 minutes). These products exhibit 0.02 %w/w Na_2O and 0.2 %w/v sulfate relative to 72.5 %w/w Al_2O_3 as the primary contaminants. US 4,154,812 describes the porosity of the boehmitic alumina as being influenced by the pH value, concentration and temperature. At the arising pH value of 2 to 5, or 3 to 4, partial hydrolysis of the acidic aluminum salt produces boehmitic alumina in the form of crystals given a high dilution and a temperature of 140 to 170 °F. These crystals act as nuclei during the subsequent precipitation. Obtained in this way are boehmitic silica that exhibit pore volumes of 0.8 to 0.9 ml/g.

US 4,248,852 describes a procedure for manufacturing γ -alumina with a high pore volume. According to this publication, aluminum salts and aluminates are reacted in such a way that several reaction phases with respectively different pH values (pH-swing) must be traversed.

The object of this invention is to manufacture alumina hydrates with crystallite sizes of 3 to 5 nm and pore volumes exceeding 1.0 ml/g, preferably exceeding 1.25 ml/g, especially preferred exceeding 1.6 ml/g by neutralizing basic aluminate solutions. The object of the invention is also to provide a procedure that makes it possible to generate products with an adjustable pore radius distribution, pore size and specific surface. In addition, the procedure according to the invention must be easy to execute, and not involve the complicated sequence of varying procedural steps known from prior art.

It was surprisingly shown that adding inorganic and organic particles, whose average particle sizes lie in the nanometer range in the receiver of the precipitate influences precipitation in such a way that the precipitated boehmitic alumina hydrates exhibit a pore volume of 1.0 to 2.5, in particular of 1.0 to 1.6 ml/g, and an average pore radius of 6 to 12 nm. This is made all the more remarkable by the fact that the inorganic particles used as the crystal nuclei themselves only exhibit a pore volume in the area of 0.5 ml/g.

The procedure according to the invention is characterized in that the precipitate comprised of aqueous solutions of an acidic aluminum salt and a basic aluminate solution in an aqueous receiver containing

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- alumina hydrate and/or alumina, which exhibits average particle diameters in aqueous media of 12 to 250 nm, preferably 20 to 150 nm, and especially preferred 20 to 100 nm, or
- 0.1 to 5 %w/w of organic polymers or oligomers relative to the precipitated alumina hydrates and computed as Al_2O_3 , which exhibit particle sizes of 12 to 250 nm, and especially preferred 20 to 150 nm or 50 to 100 nm, or
- any mixtures of the latices and alumina/alumina hydrate particles described above.

10 In the procedure according to the invention, alumina hydrates with a very high pore volume (as determined per DIN 66134) and an average pore radius of 6 to 12 nm (as determined per DIN 66134) are accessible at a crystallite size of 3 to 5 nm as determined via X-ray diffraction on a 120 reflex.

15 The procedure is preferably executed in such a way that

- the crystal nuclei are presented in an aqueous acidic solution, and
- one or more basic aluminum salts, e.g., alkaline or earth-alkaline aluminates and one or more acidic aluminum salts (including aluminum oxy salts), e.g., aluminum sulfate, aluminum nitrate, aluminum chloride, aluminum formiate or aluminum oxy chloride or aluminum oxy nitrate, are added, preferably essentially together, or
- the basic aluminum compound is precipitated by adding an aqueous acid, or the acidic aluminum compound is precipitated by adding an aqueous base.

25 The crystal nuclei comprised of alumina hydrates and/or alumina, which in aqueous media exhibit average particle diameters of 12 to 250 nm, preferably 20 to 150 nm, and especially preferred 50 to 100 nm, themselves generally consist of agglomerates of crystallites, which preferably exhibit relatively high crystallite sizes exceeding 4 nm, preferably between 4 and 40 nm.

30 Precipitation preferably takes place from aqueous dispersions of alumina particles with the addition of 0.1 to 5 %w/w of the inorganic crystal nuclei, preferably 0.5 to 2 %w/w and especially preferred 1 to 1.5 %w/w relative to the Al_2O_3 to be precipitated in all.

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However, the precipitation can also take place from aqueous dispersions of organic compounds described above, which form latices in the precipitation medium.

5 In terms of the invention, latex is a colloidal dispersion of organic polymers or oligomers in an aqueous medium. Suitable for the creation of latices are polymers or oligomers that exhibit a carbon chain of more than 20, preferably more than 100 carbon atoms as the basic framework, and additionally are preferably fabricated out of monomer units containing at least one double bond, preferably a vinyl or acrylic double bond. These include the following polymers/oligomers: Polystyrene, 10 polyacrylic acid, polymethacrylic acid and polyvinyl acetate, along with their copolymers and mixtures. Suitable compositions include those available from the company Neste Chemicals GmbH under the trade name Dilexo.

15 In this embodiment, the organic compounds are used in an amount of 0.1 to 5 %w/w, preferably 0.5 to 2 %w/w, and especially preferred 1 to 1.5 %w/w, relative the total alumina hydrate to be precipitated (determined as Al_2O_3).

20 Precipitation takes place in an aqueous receiver that consists of a dispersion of inorganic or organic particles, or a mixture of an acidic aluminum salt and a dispersion of inorganic or organic particles. Precipitation preferably takes place at a temperature of 20 to 98 °C, especially preferred 60 to 80 °C. The bulk of the alumina hydrate is precipitated at a pH value of 5 to 9, especially preferred 6 to 8.

25 The alumina hydrates manufactured according to the invention exhibit a distinctly lower content of anionic (e.g., sulfate) and cationic (e.g., sodium) contaminants than conventionally fabricated ones.

30 Gibbsite, Nordstrandite, amorphous alumina, Bayerite and diasporite can be used as the crystal nuclei, with boehmitic and/or pseudo-boehmitic alumina being preferred.

35 The crystal nuclei that can be used according to the invention are accessible according to the procedure described in DE 38 23 395-C1, for example. In this procedure, boehmitic alumina with an average pore radius of 3 to 100 nm can be manufactured via the hydrothermal ageing of an alumina suspension obtained via the hydrolysis of aluminum alkoxides. Hydrothermal ageing causes the crystallite sizes to grow to up to 40 nm in the respective spatial directions. The pore volume of these boehmitic aluminas ranges from 0.6 to 0.8 ml/g. However, a procedure

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according to DE 43 37 643-C1 is better suited for the manufacture of the crystal nuclei useable according to the invention. When using crystal nuclei fabricated according to this procedure, precipitation products with higher pore volumes are obtained. The disclosure in DE 43 37 643-C1 will hereby expressly be included in the contents of this application.

The organic compounds do not act as opening materials, which are known for the fabrication of ceramics. The organic compounds used according to the invention are added in small quantities relative to these applications, while the opening materials are added primarily in quantities exceeding 10 %w/w. As opposed to the receiver of organic particles, the alumina hydrates according to this embodiment exhibit a higher content of anionic contaminants.

Alumina hydrates obtainable according to this procedure are preferably boehmitic or pseudo-boehmitic aluminas.

Experimental Section:

The crystallite sizes of the boehmitic aluminas were determined at 120 reflex using the general Scherrer formula:

$$\text{Crystallite size} = (K \times \lambda \times 57.3) / (\beta \times \cos \theta)$$

K (form factor): 0.992; λ (wavelength of X-ray radiation): 0.154 nm; β (corrected industrial broadening of spectral lines): reflex-dependent; θ : reflex-dependent.

The measurements were performed on an X'pert-type XRD device made by Philips. Measuring parameters: start angle [$^{\circ}2\theta$]: 5.010; end angle [$^{\circ}2\theta$]: 79.990; start d-value [\AA]: 17.62435; end d-value [\AA]: 1.19850; anode material: Cu; $\alpha 1$ wavelength [\AA]: 1.54060; $\alpha 2$ wavelength [\AA]: 1.54439.

The pore size distribution, overall pore volume and specific surface are determined via nitrogen adsorption according to DIN 66134 with a device from the Quantachrome company. The contaminants were determined via atomic emission spectroscopy with inductively coupled plasma (AES-ICF, SPECTRO company).

Example 1 (Comparison Example)

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31.6 kg of water were heated to 70 °C in a 350 l mixing vessel equipped with stirring system, heating jacket and pH measuring device. An aluminum sulfate solution was added (6.2 % Al_2O_3) until a pH value of 3.5 was established. Mixing took place for 5 minutes under these conditions (62 RPM). Subsequently, the aluminum sulfate solution (2.16 l/h) and a sodium aluminate solution (21.1 % Al_2O_3 , 16.8 l/h) were simultaneously added while mixing to set a pH value of 7.3. The precipitated boehmitic alumina was filtered out, washed with fully desalinized water (50 g water/g alumina), and dried with a spray dryer (air outlet temperature 120 °C).

After activated for 3 h at 550 °C, the product obtained according to the comparison example exhibits the pore size distribution indicated in Table 1, an overall pore volume (0 to 100 nm) of 0.89 ml/g, and a specific surface of 280 m^2/g . In this case, the average pore radius measured 5.8 nm. The crystallite size determined on the 120 reflex measured 4 nm. Contaminants were determined via atomic emission spectroscopy with inductively coupled plasma (ABS-ICP, SPECTRO company). In this case, a Na content of 132 ppm and sulfate content of 0.12 % was obtained at an Al_2O_3 content of 72.5 %.

Example 2

1.23 kg of a 65 % nitric acid followed by 1.43 g of PURAL SB-1 (CONDEA) were mixed into 98.77 kg of water to manufacture an alumina sol. The average size of the alumina particles in the sol measures 65 nm.

To precipitate the boehmitic alumina, the alumina sol is heated to 70 °C. The pH value is subsequently raised by adding sodium aluminate solution (21.1 % Al_2O_3 , 16.8 l/h) and set to 7.3 via the simultaneous addition of aluminum sulfate solution (6.2 % Al_2O_3 , 21.6 l/h). The precipitated boehmitic alumina was filtered off, washed with fully desalinized water (50 g water/g alumina), and dried with a spray dryer (air outlet temperature 120 °C).

The pore size distribution, overall pore volume, specific surface and contaminants were determined based on the method described in the experiment section. After activated for 3 h at 550 °C, the product obtained according to Example 2 exhibits the pore size distribution indicated in Table 2, an overall pore volume (0 to 100 nm) of 1.33 ml/g, and a specific surface of 274 m^2/g . In this case, the average pore

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radius measured around 12 nm. The crystallite size determined on the 120 reflex measured 4 nm, the Na content 58 ppm, and the sulfate content 504 ppm.

Example 3

5

20 kg of glacial acetic acid followed by 1.43 kg of DISPERAL ® sol P3 (CONDEA) were mixed into 80 kg of water to manufacture an alumina sol. The average size of the alumina particles in the sol measured 22 nm.

10

To precipitate the boehmitic alumina, the alumina sol was heated to 70 °C. The pH value was subsequently raised by adding sodium aluminate solution (21.1 % Al_2O_3 , 16.8 l/h) and set to 7.3 via the simultaneous addition of aluminum sulfate solution (6.2 % Al_2O_3 , 21.6 l/h). The precipitated boehmitic alumina was filtered off, washed with fully desalinized water (50 g water/g alumina), and dried with a spray dryer (air outlet temperature 120 °C).

15

20

The pore size distribution, overall pore volume, specific surface and contaminants were determined based on the method described in the experiment section. After activated for 3 h at 550 °C, the product obtained according to Example 3 exhibited an overall pore volume (0-100 nm) of 1.46 ml/g and a specific surface of 277 m^2/g . In this case, the average pore radius measured around 10 nm. The crystallite size determined on the 120 reflex measured 4 nm. The Na content measured 53 ppm, and the sulfate content 539 ppm.

25

Example 4

1 kg of formic acid followed by 1.43 kg of CATAPAL A (CONDEA Vista) were mixed into 99 kg of water to manufacture an alumina sol. The average size of the alumina particles in the sol measured 90 nm.

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To precipitate the boehmitic alumina, the alumina sol was heated to 70 °C. The pH value was subsequently raised by adding sodium aluminate solution (21.1 % Al_2O_3 , 16.8 l/h) and set to 7.3 via the simultaneous addition of aluminum sulfate solution (6.2 % Al_2O_3 , 21.6 l/h). The precipitated boehmitic alumina is filtered off, washed with fully desalinized water (50 g water/g alumina), and dried with a spray dryer (air outlet temperature 120 °C).

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The pore size distribution, overall pore volume, specific surface and contaminants are determined based on the method described in the experiment section. After activated for 3 h at 550 °C, the product obtained according to Example 4 exhibits an overall pore volume (0-100 nm) of 1.25 ml/g and a specific surface of 277 m²/g. In this case, the average pore radius measures around 11 nm. The crystallite size determined on the 120 reflex measured 4 nm, the Na content 126 ppm, and the sulfate content 464 ppm.

Example 5

1.23 kg of 65 % nitric acid followed by 1.43 kg of PURAL 200 (CONDEA) were mixed into 98.77 kg of water to manufacture an alumina sol. The average size of the alumina particles in the sol measures 240 nm.

To precipitate the boehmitic alumina, the alumina sol is heated to 70 °C. The pH value is subsequently raised by adding sodium aluminate solution (21.1 % Al₂O₃, 16.8 l/h) and set to 7.3 via the simultaneous addition of aluminum sulfate solution (6.2 % Al₂O₃, 21.6 l/h). The precipitated boehmitic alumina is filtered off, washed with fully desalinated water (50 g water/g alumina), and dried with a spray dryer (air outlet temperature 120 °C).

The pore size distribution, overall pore volume, specific surface and contaminants were determined based on the method described in the experiment section. After activated for 3 h at 550 °C, the product obtained according to Example 5 exhibits an overall pore volume (0-100 nm) of 0.98 ml/g and a specific surface of 279 m²/g. In this case, the average pore radius measured around 7 nm. The crystallite size determined on the 120 reflex measured 4 nm, the Na content 42 ppm, and the sulfate content 0.1 %.

The pore properties of the aluminas obtained according to examples 2 to 5 are summarized in Table 1 as a function of the average particle size in the prepared sol:

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Table 1

Average particle size	Pore volume	Average pore radius in sol (0-100 nm)
22 nm	1.46 ml/g	10 nm
65 nm	1.55 ml/g	12 nm
90 nm	1.25 ml/g	11 nm
240 nm	0.98 ml/g	7 nm

As evident, a maximal pore volume and a maximal average pore radius can be
5 achieve in the area of a sol with a particle size of 65 nm in the aqueous receiver.

Example 6

2.2 kg of a polymer dispersion consisting of acrylic acid and methacrylic acid
10 (DILEXO MM 16, NESTE Chemicals GmbH, Düsseldorf) were mixed into 90 kg of
water. The average particle size in the dispersion measured 39 nm.

To prepare the precipitate, the polymer dispersion was set to a pH of 3.5 by adding
aluminum sulfate solution drop-by-drop and heated to 70 °C. To precipitate the
15 boehmitic alumina, the pH value was raised by adding sodium aluminate solution
(21.1 % Al_2O_3 , 16.8 l/h) and set to 7.3 via the simultaneous addition of aluminum
sulfate solution (6.2 % Al_2O_3 , 21.6 l/h). The precipitated boehmitic alumina was
filtered off, washed with fully desalinized water (50 g water/g alumina), and dried
with a spray dryer (air outlet temperature 120 °C).

20 The pore size distribution, overall pore volume, specific surface and contaminants
were determined based on the method described in the experiment section. After
activated for 3 h at 550 °C, the product obtained according to Example 6 exhibited
an overall pore volume (0-100 nm) of 1.20 ml/g and a specific surface of 325 m^2/g .
25 In this case, the average pore radius measured around 7 nm. The crystallite size
determined on the 120 reflex measured 4 nm, the Na content 94 ppm, and the
sulfate content 1.0 %.

- 10 -

Example 7

2.2 kg of a polymer dispersion consisting of acrylic acid and methacrylic acid (DILEXO MM 16, NESTE Chemicals GmbH, Düsseldorf) were mixed into 90 kg of water. The average particle size in the dispersion measured 39 nm.

To prepare the precipitate, the polymer dispersion was set to a pH of 3.5 by adding aluminum sulfate solution drop-by-drop and heated to 70 °C. To precipitate the boehmitic alumina, the pH value was lowered by adding aluminum sulfate solution (6.2 % Al_2O_3 , 21.6 l/h) and set to 7.3 via the simultaneous addition of sodium aluminate solution (21.1 % Al_2O_3 , 16.8 l/h). The precipitated boehmitic alumina was filtered off, washed with fully desalinized water (50 g water/g alumina), and dried with a spray dryer (air outlet temperature 120 °C).

The pore size distribution, overall pore volume, specific surface and contaminants were determined based on the method described in the experiment section.

After activated for 3 h at 550 °C, the product obtained according to Example 7 exhibited an overall pore volume (0-100 nm) of 1.20 ml/g and a specific surface of 299 m^2/g . In this case, the average pore radius measured around 7 nm. The crystallite size determined on the 120 reflex measured 3 nm, the Na content 72 ppm, and the sulfate content 1.0 %.

The alumina hydrates manufactured in examples 1 to 7 exhibit the pore radius distribution, pore volumes and pore surface exhibited in Table 2.

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Table 2

Example 1		Example 2		Example 3	
Radius	Pore vol.	Radius	Pore vol.	Radius	Pore vol.
Å	[cc/g]	Å	[cc/g]	Å	[cc/g]
11.53	0.00E+00	11.48	0.00E+00	11.6	0.00E+00
13.32	0.00E+00	13.25	0.00E+00	13.26	0.00E+00
14.09	0.00E+00	14.08	0.00E+00	14.02	0.00E+00
14.9	0.00E+00	14.77	0.00E+00	14.83	0.00E+00
15.72	0.00E+00	15.62	0.00E+00	15.68	0.00E+00
16.48	0.00E+00	16.52	0.00E+00	16.59	0.00E+00
17.45	0.00E+00	17.48	0.00E+00	17.55	0.00E+00
18.43	0.00E+00	18.46	0.00E+00	18.55	0.00E+00
19.45	0.00E+00	19.46	0.00E+00	19.52	0.00E+00
20.78	1.34E-03	20.74	0.00E+00	20.77	0.00E+00
22.22	4.86E-03	22.14	0.00E+00	22.09	0.00E+00
23.65	1.12E-02	23.68	0.00E+00	23.43	0.00E+00
25.2	2.43E-02	25.35	2.64E-04	25.16	0.00E+00
27.11	5.96E-02	27.03	1.71E-03	27.15	0.00E+00
29.3	1.30E-01	29.06	6.25E-03	29.27	3.95E-03
31.67	2.59E-01	31.45	1.18E-02	31.49	1.63E-02
34.34	4.18E-01	34.21	3.19E-02	34.07	5.28E-02
36.46	4.79E-01	36.3	3.97E-02	36.27	8.50E-02
37.78	5.25E-01	37.43	5.34E-02	37.66	1.17E-01
38.9	5.70E-01	38.94	7.13E-02	38.98	1.63E-01
40.32	6.11E-01	40.51	9.29E-02	40.55	2.27E-01
42.08	6.44E-01	42.04	1.21E-01	42.3	3.06E-01
43.85	6.69E-01	43.91	1.62E-01	43.92	3.62E-01
45.83	6.94E-01	45.89	2.02E-01	45.74	4.15E-01
47.8	7.09E-01	47.93	2.45E-01	47.95	4.87E-01
49.89	7.29E-01	50.24	3.06E-01	50.15	5.43E-01
52.56	7.52E-01	52.73	3.64E-01	52.48	6.07E-01
54.97	7.60E-01	55.27	4.19E-01	55.15	6.61E-01
57.35	7.76E-01	58.24	4.88E-01	58.31	7.25E-01
60.87	7.89E-01	61.61	5.42E-01	61.46	7.81E-01
64.24	7.97E-01	65.19	5.97E-01	65.02	8.42E-01
68.48	8.10E-01	69.45	6.70E-01	69.05	8.84E-01
73.65	8.17E-01	74.02	7.20E-01	73.86	9.35E-01
78.69	8.24E-01	79.49	7.77E-01	79.4	9.78E-01
84.41	8.30E-01	85.94	8.40E-01	85.09	1.02E+00
90.71	8.36E-01	92.9	8.95E-01	92.49	1.08E+00
98.16	8.42E-01	101.74	9.58E-01	101.15	1.12E+00
108.02	8.47E-01	112.74	1.02E-00	112.23	1.17E+00
120.49	8.52E-01	126.63	1.08E-00	125.42	1.20E+00
135.88	5.57E-01	143.35	1.14E-00	142.44	1.23E+00
155.57	8.62E-01	164.42	1.20E-00	168.89	1.26E+00
182.4	8.67E-01	195.37	1.26E-00	190.43	1.30E+00
223	8.72E-01	241.94	1.32E-00	231.5	1.33E+00
294.58	8.77E-01	323.12	1.39E-00	297.27	1.37E+00
420.95	8.83E-01	454.54	1.44E-00	432.76	1.42E+00
651.25	8.88E-01	809.41	1.52E-00	701.87	1.46E+00
1173.10	8.92E-01	1429.05	1.55E-00	1007.56	1.46E+00

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Table 2 (continuation)

Example 4		Example 5	
Radius	Pore vol.	Radius	Pore vol.
Å	[cc/g]	Å	[cc/g]
11.42	0.00E+00	11.53	0.00E+00
13.1	2.03E-04	13.21	0.00E+00
13.84	4.84E-04	13.96	0.00E+00
14.62	8.55E-04	14.76	0.00E+00
15.45	8.55E-04	15.61	0.00E+00
16.34	1.43E-03	16.53	0.00E+00
17.29	1.99E-03	17.5	0.00E+00
18.31	2.76E-03	18.54	0.00E+00
19.42	3.66E-03	19.62	0.00E+00
20.62	4.66E-03	20.67	0.00E+00
21.95	5.28E-03	22.07	8.42E-04
23.43	7.13E-03	23.6	2.46E-03
25.05	9.32E-03	25.06	7.19E-03
26.81	1.20E-02	26.81	1.43E-02
28.6	1.44E-02	29.04	3.27E-02
31.07	2.13E-02	31.52	6.26E-02
33.73	2.74E-02	34.19	1.30E-01
35.5	3.11E-02	36.38	1.72E-01
36.86	3.62E-02	37.74	2.19E-01
38.27	4.16E-02	39.01	2.76E-01
39.8	4.70E-02	40.42	3.50E-01
41.38	5.4E-02	42.18	4.31E-01
42.86	6.07E-02	43.99	5.02E-01
44.02	7.54E-02	45.86	5.77E-01
47.43	8.54E-02	47.73	6.20E-01
49.24	9.49E-02	49.82	6.82E-01
51.54	1.15E-01	52.22	7.22E-01
54.56	1.35E-01	54.67	7.53E-01
57.72	1.60E-01	57.77	7.84E-01
60.69	1.83E-01	60.98	8.03E-01
64.47	2.22E-01	64.49	8.22E-01
68.87	2.59E-01	67.94	8.32E-01
73.48	3.17E-01	72.52	8.48E-01
78.91	3.69E-01	78.39	8.57E-01
84.69	4.43E-01	84.04	8.66E-01
93.44	5.16E-01	90.57	8.74E-01
102.31	6.05E-01	98.5	8.81E-01
112.48	6.82E-01	108.29	8.88E-01
125.17	7.70E-01	120.35	8.96E-01
141.76	8.55E-01	135.46	9.03E-01
161.22	9.36E-01	154.42	9.09E-01
190.61	1.03E+00	177.26	9.16E-01
232.53	1.09E+00	226.1	9.28E-01
294.97	1.15E+00	301.37	9.36E-01
440.19	1.20E+00	453.46	9.51E-01
767.58	1.23E+00	857.48	9.68E-01
1530.56	1.25E+00	1497.5	9.76E-01

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Table 2 (continuation)

Example 6		Example 7	
Radius	Pore vol.	Radius	Pore vol.
Å	[cc/g]	Å	[cc/g]
11.64	00.00E+00	11.51	0.00E+00
13.34	00.00E+00	13.23	0.00E+00
14.11	00.00E+00	13.89	0.00E+00
14.95	00.00E+00	14.72	0.00E+00
15.81	00.00E+00	15.65	0.00E+00
16.7	00.00E+00	16.41	0.00E+00
17.6	00.00E+00	17.26	0.00E+00
18.61	00.00E+00	18.45	0.00E+00
19.71	5.42E-04	19.57	0.00E+00
20.96	2.71E-03	20.67	7.98E-05
22.33	8.35E-03	22.05	1.68E-03
23.72	1.95E-02	23.48	4.57E-03
25.38	4.11E-02	25.13	1.34E-02
27.22	7.72E-02	27.09	2.72E-02
29.29	1.37E-01	29.12	4.50E-02
31.68	2.49E-01	31.53	7.46E-02
34.38	4.03E-01	34.18	1.18E-01
36.44	4.65E-01	36.1	1.47E-01
37.77	5.25E-01	37.59	1.90E-01
39.13	5.73E-01	39.18	2.48E-01
40.59	6.18E-01	40.51	2.95E-01
42.22	6.52E-01	42.1	3.82E-01
43.92	6.85E-01	44.09	4.59E-01
45.83	7.13E-01	45.93	5.49E-01
47.88	7.37E-01	47.92	6.28E-01
50.2	7.61E-01	50.08	6.98E-01
52.61	7.82E-01	52.46	7.58E-01
55.02	8.02E-01	55.2	8.13E-01
57.99	8.25E-01	58.04	8.60E-01
61.48	8.45E-01	61	8.91E-01
64.97	8.66E-01	64.59	9.22E-01
69.06	8.91E-01	69.06	9.46E-01
74.04	9.18E-01	73.47	9.64E-01
79.61	9.49E-01	78.2	9.80E-01
85.86	9.79E-01	84.07	9.96E-01
93.22	1.02E+00	92.31	1.02E+00
102.36	1.05E+00	102.41	1.03E+00
113.32	1.07E+00	111.74	1.04E+00
125.91	1.09E+00	123.75	1.06E+00
141.67	1.11E+00	137.64	1.06E+00
164.7	1.12E+00	161.76	1.08E+00
193.16	1.14E+00	190.92	1.09E+00
238.94	1.15E+00	230.14	1.10E+00
307.19	1.17E+00	299.79	1.11E+00
447.68	1.18E+00	453.25	1.13E+00
698.1	1.19E+00	737.46	1.16E+00
1007.91	1.19E+00	1367.11	1.18E+00

ART 34 AMOT

D-99 004 PCT

Claims as amended in Ch.II proceedings

D-99004 PCT

CLAIMS

5

1. A procedure for manufacturing boehmitic and/or pseudo-boehmitic alumina by precipitating basic and/or acidic aluminum salts, characterized by the fact that precipitation takes place from an aqueous medium containing the following as the crystal nuclei:

10

(a) 0.1 to 5 %w/w of alumina hydrates and/or aluminas relative to the precipitated alumina hydrates and computed as Al_2O_3 , wherein the crystal nuclei (a) in the medium exhibit an average diameter of 20 to 150 nm.

15

2. The procedure for manufacturing alumina hydrates by precipitating basic and/or acidic aluminum salts, characterized in that precipitation takes place from an aqueous medium containing the following as the crystal nuclei:

20

(b) 0.1 to 5 %w/w of organic polymers/oligomers relative to the precipitated alumina hydrates and computed as Al_2O_3 , which form lattices in the medium, wherein the crystal nuclei (b) in the medium exhibit an average diameter of 12 to 250 nm.

25

3. The procedure according to one of the preceding claims, characterized in that crystal nuclei exhibit an average diameter of 20 to 150 nm, preferably 50 to 100 nm.

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4. The procedure according to one of the preceding claims, characterized in that crystal nuclei in an amount of 0.5 to 2 %w/w relative to the precipitated alumina hydrates and computed as Al_2O_3 are used for precipitation.

35

5. The procedure according to one of the preceding claims, characterized in that

- the crystal nuclei are prepared in an aqueous, acidic solution and
- one or more basic aluminum salts and one or more acidic aluminum salts are jointly added.

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Claims as amended in Ch. II proceedings

- 5 6. The procedure according to one of the preceding claims, characterized in that polyacrylic acids, polymethacrylic acid, polyacrylates, polystyrenes, polyvinyl acetates, polyvinyl versalates and their mixtures or copolymers are used as organic polymers.
- 10 7. The procedure according to one of the preceding claims, characterized in that alkali aluminates, earth alkali aluminates or aluminum hydroxy salts are used as the basic aluminum salts.
- 15 8. The procedure according to one of the preceding claims, characterized in that aluminum sulfate, aluminum nitrate, aluminum chloride or aluminum formate are used as the acidic aluminum salts.
- 20 9. The procedure according to one of the preceding claims, characterized in that the bulk of the alumina hydrate is precipitated at a pH value of 5 to 9, especially preferred 6 to 8.
- 25 10. The procedure according to one of the preceding claims, characterized in that the crystal nuclei (a) and (b) are used jointly.
- 30 11. A boehmitic alumina and/or pseudo-boehmitic alumina with a pore volume of 1.25 to 1.6 ml/g and an average pore radius of 6 to 12 nm, each relative to a determination based on pore radii of 0 to 100 nm, at a crystallite size, determined on the 120 reflex, of 3 to 5 nm, manufactured according to a procedure described in the preceding claims.

35

D99004_PCT_Engl

SS

ABSTRACT

The invention relates to a procedure for manufacturing alumina hydrates by precipitating aluminum salts in the presence of crystal nuclei of a specific size.

- nicht weitergereicht -

2025040 040202

Docket No.

Mueller-41

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Method of Producing Aluminum Hydroxides by Precipitating Aluminum Salts in the Presence of Seed Crystals

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on January 4, 2002 as United States Application No. or PCT International

Application Number 10/019,795

and was amended on _____

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

19930924.8

Germany

6 July 1999

☐

(Number)

(Country)

(Day/Month/Year Filed)

☐

(Number)

(Country)

(Day/Month/Year Filed)

☐

(Number)

(Country)

(Day/Month/Year Filed)

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

PCT/DE00/02138

5 July 2000

Pending

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

#5

JC02 Rec'd PCT/PTO 02 APR 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
ACTING AS RECEIVING OFFICE FOR THE PCT

10/019795

In re Application of:	§	Attorney Docket No.: Muller-41
	§	
Rainer Gloeckler and Arnold Meyer	§	U.S. Serial No.: 10/019,795
	§	
Int'l. Appln. No.: PCT/DE00/02138	§	U.S. Filing Date: January 04, 2002
	§	
Int'l. Filing Date: 05 July 2000	§	Art Unit No. To Be Assigned
	§	
Priority Date: 06 July 1999	§	Examiner: To Be Assigned
	§	
For: <i>Method of Producing Aluminum</i>	§	
<i>Hydroxides by Precipitating</i>	§	
<i>Aluminum Salts in the Presence</i>	§	
<i>of Seed Crystals</i>	§	

TRANSMITTAL LETTER

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn.: DO/EO/US

Sir:

Enclosed for filing in the above-identified application are the following:

1. Response to Notification of Missing Requirements Under 35 U.S.C. §371 in the United States Designated/Elected Office (DO/EO/US) (1 page);
2. Copy of Notification of Missing Requirements (1 page);
3. Declaration and Power of Attorney (4 pages);
4. Check in the amount of \$250 for the combined Declaration surcharge of \$130 and the additional claim fees of \$120;
6. Acknowledgment postcard; and

04/08/2002 MNGUYEN 00000023 10019795

01 FC:154	130.00 OP
02 FC:966	36.00 OP
03 FC:964	84.00 OP

202040" 96257001

7. Duplicate copies of this transmittal letter for the Assistance Commissioner's use in crediting overpayment or charging any additional fees due to Deposit Account No. 02-4345.

Respectfully submitted,



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CERTIFICATE OF EXPRESS MAILING

I, C. James Bushman, hereby certify that this correspondence and all referenced enclosures are being deposited by me with the United States Postal Service as Express Mail with Receipt No. EL715549416US in an envelope addressed to: Box PCT, Assistant the Commissioner for Patents, U.S. Patent and Trademark Office, Washington D.C. 20231, on April 2, 2002.

By: 

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